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13. ABSTRACT (*Maximum 200 words*)

This contract addressed the issue of the spectral selectivity of emitters in thermophotovoltaic electric generators. In these systems, a fuel is burned to heat an emitter, which radiates energy to photovoltaic cells. One critical factor in overall system efficiency and output power is the percentage of radiant energy within the band of the photovoltaic cells. This contract investigated various emitter coatings in order to maximize radiant energy within the band of the photovoltaic cells being used, while minimizing the out-of-band energy.

An appropriate coating sequence has been identified and successfully tested. The goal was to tune the spectrum for gallium antimonide photovoltaic cells, because these cells respond to longer wavelengths than traditional photovoltaic cells, and because these cells are practical to manufacture. Of the refractory metals investigated, tungsten proved to be the most stable. With an anti-reflective coating over the tungsten, the spectrum can be finely tuned for the 1.8 micron band-edge of gallium antimonide cells.

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DARPA/ARO Final Report
Contract #DAAD19-99-C-0034

JX Crystals Inc.
James E. Avery & Dr. Lewis M. Fraas

May 22, 2000

Summary

This contract addressed the issue of the spectral selectivity of emitters in thermophotovoltaic electric generators. In these systems, a fuel is burned to heat an emitter, which radiates energy to photovoltaic cells. One critical factor in overall system efficiency and output power is the percentage of radiant energy within the band of the photovoltaic cells. This contract investigated various emitter coatings in order to maximize radiant energy within the band of the photovoltaic cells being used, while minimizing the out-of-band energy.

The results have been quite positive; an appropriate coating sequence has been identified and successfully tested. The goal was to tune the spectrum for gallium antimonide (GaSb) photovoltaic cells, because GaSb cells respond to longer wavelengths than traditional photovoltaic cells, and because GaSb cells are practical to manufacture. Of the refractory metals investigated, tungsten proved to be the most stable. With an anti-reflective coating over the tungsten, the spectrum can be finely tuned for the 1.8 micron band-edge of GaSb cells.

JX Crystals appreciates the support of DARPA and the Army Research Office in this effort, and is eager to begin the next phase of development. With an appropriate emitter identified, the company intends to work on a self-standing system using this new emitter technology. The principle requirement will be a hermetic seal of the cavity in which the emitter operates. Tungsten degrades rapidly in an atmosphere with oxygen, so the cavity must be evacuated and backfilled with an inert gas. In essence, this is light bulb technology; though it is not trivial, it is achievable.

Outline

This final report steps through all of the stages of the contract:

- Theory of Anti-Reflective/Refractory Metal (AR/RM) Emitters
- Coupon Experiments
- AR/RM Cylinder Coatings
- Burner Development
- Thermophotovoltaic (TPV) Cell & AR/RM Emitter Test Results
- Conclusions and Relation to Future Work

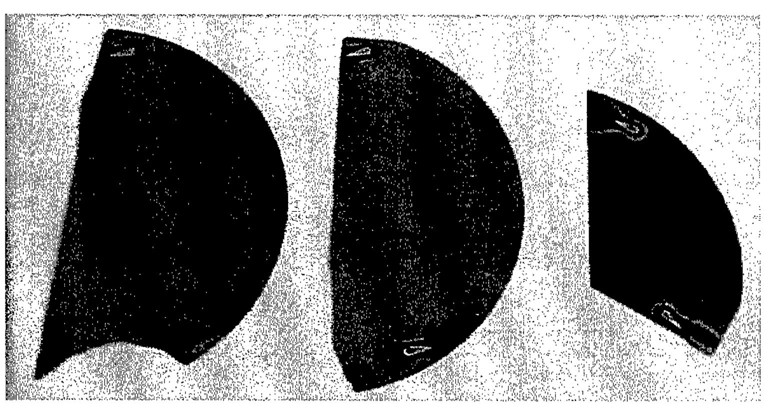
Theory of AR/RM Emitters

TPV generators convert infrared radiation from heated emitters into electric power. The infrared emitters in these units can operate at moderate temperatures between 900° C and 1400° C. Baseline TPV generators use gray-body silicon carbide (SiC) emitters with GaSb cells. The SiC emitter emits infrared energy at all wavelengths. However, the GaSb cells only convert infrared photons with wavelengths less than 1.8 microns to electric power. Infrared filters are far from perfect, but they are used to reflect some of the non-useful longer wavelength photons back to the emitter.

It is preferable to replace the gray-body emitter with a "matched" infrared emitter that only emits convertible infrared radiation. Mathematically, this perfect "matched" emitter would have an emittance of 1.0 for wavelengths less than 1.8 microns and 0 for longer wavelengths. Several prior art infrared emitters have been proposed for use in TPV generators. Rare earth oxide emitters such as erbia have a narrow emittance bandwidth below 1.8 microns, but a comparatively large amount of out-of-band energy. Cobalt-doped emitters have a wider in-band emittance bandwidth, but they tend to crack after extensive thermal cycling. Finally, tungsten emitters have been considered, but tungsten has the drawback of low emissivity in-band. Still, tungsten is selective, because the out-of-band emissivity is even lower.

This contract investigated the use of anti-reflective (AR) coatings on tungsten and on other refractory metals, in order to enhance the in-band emissivity of the metals. Tungsten (W) proved to be the most durable material, and is the focus of this report. Test results on other materials were provided in monthly reports, and are not repeated here.

It was desirable to develop a simple test of the theory that the emissivity of tungsten could be tailored with an AR coating. Coating a few samples and measuring their reflectance achieved this. Emissivity equals one minus reflectance for a given temperature (for instance, a blackbody does not reflect at any wavelength; it has an emissivity of 1.0 at all wavelengths). So, pieces of silicon were coated with tungsten and varying levels of AR coating. These are shown below in figure 1.



133 nm AR *145 nm AR* *170 nm AR*

Figure 1. Varying thicknesses of AR-coating on tungsten on silicon wafers

The samples shown in figure 1 are visibly distinct, but the wavelengths of interest for TPV applications are beyond the visible range. Based on known room temperature n and k data for tungsten, a theoretical model was developed to estimate the optimal AR-coating thickness at 1200° C; this model is shown in figure 2. Using JX Crystals' custom dispersive spectrometer for the 1–5.4 micrometer wavelength range, reflectance was measured at room temperature, reasonably matching the model below. As expected, an AR coating vastly improved the emissivity of tungsten below 1.8 microns. The bottom line is tungsten without any coating; adding an AR-coating gradually improves selectivity up to a thickness in the range of 120-160 nanometers. This is the standard thickness range used on future tests of AR-coated tungsten under this effort. Thinner coatings lower the emissivity peak.

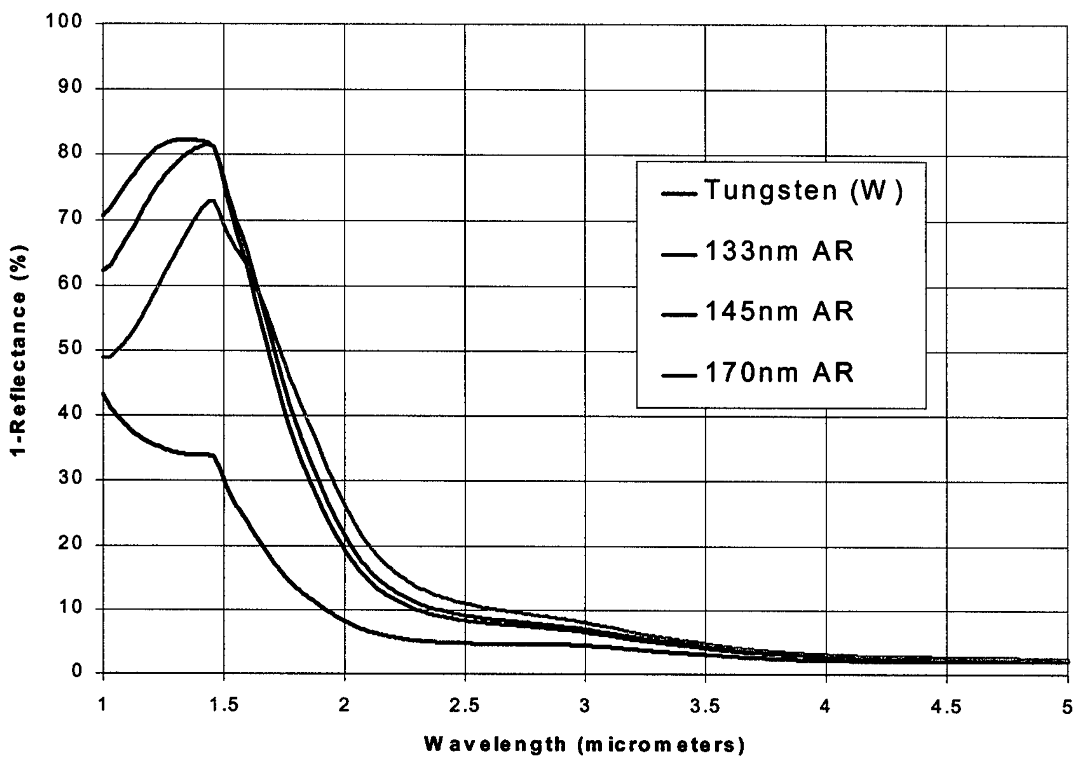


Figure 2. Emittance equals 1.0 – Reflectance, this theoretical model was used to determine optimal AR-coating thicknesses

The results shown in figure 2 verified that an AR-coating enhances the spectral selectivity of tungsten at room temperature. The next step was to see if AR-coated tungsten would adhere to appropriate emitter materials, survive at operating temperatures, and maintain its spectral properties.

Coupon Experiments

Tungsten was sputter-coated onto silicon carbide (SiC) and Kanthal (an alloy of Iron, Chrome and Aluminum) coupons measuring 2" x 2". These tungsten-coated coupons were then coated with various anti-reflective coatings. These coupons were heated in a high vacuum furnace with no discernable degradation. Then, these coupons were put into a custom spectral test unit built by JX Crystals, and emissivity was measured with good results. Limitations on how hot the test system could get the coupons limited the results, so another test was devised to measure emissivity at TPV operating temperatures. Test results were quite good, but not as positive as the theory from figure 2. Operation at temperature shifted the emissivity to slightly longer wavelengths. Coupon test results and the TPV operating temperature test results are provided after the pictures and descriptions of the equipment that was used.

Figures 3-6 show the equipment used for fabrication and testing. The tabletop sputtering system (figure 3) allowed the company to sputter material on a small surface cost-effectively. The vacuum furnace (figure 4) was used to thermal cycle the coupons up to 1400° C for life testing. Spectral measurements were made with the equipment pictured and described on the following page.

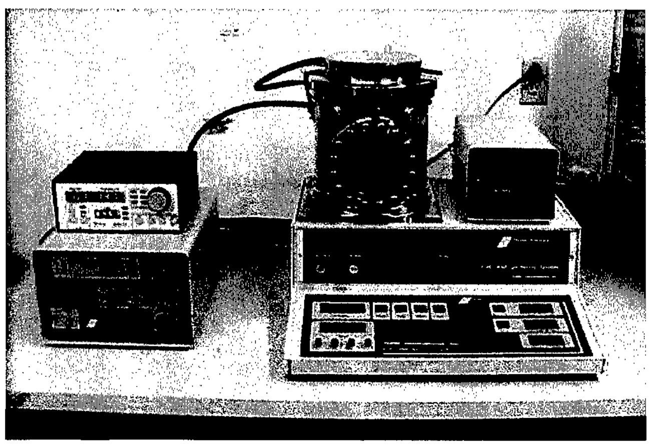


Figure 3. Tabletop Sputtering System for Coupons

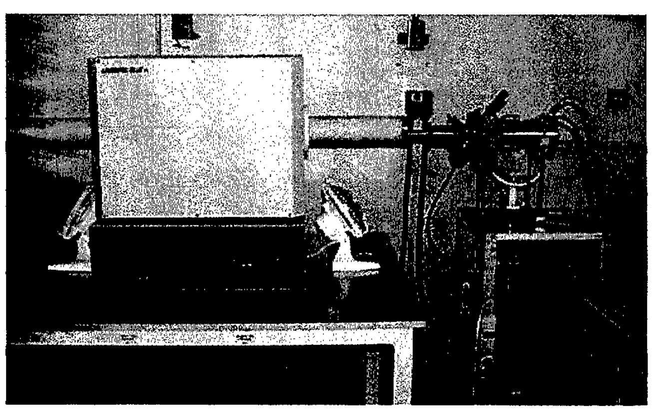


Figure 4. Vacuum Furnace for 1400° C Coupon Life Testing

Spectral measurements were made using JX Crystals' custom-made Vacuum Flat Pack test station (figure 5) incorporated into the optics bench (figure 6). The Flat Pack allows 2" x 2" coupons to be heated under vacuum. A coupon in the Flat Pack is heated from behind by SiC hot-surface ignitors, which limits the coupon temperature to no more than 1000° C. The coupon is mounted inside the Flat Pack with the coated surface facing the viewport. The spectroscopy system is used to take spectral measurements of the coated surface through the viewport. While 1000° C is below typical TPV operating temperatures, it provided the company with verification that the material is still spectrally selective at highly elevated temperatures. Another test is described later in this section that addressed operation at 1300° C.

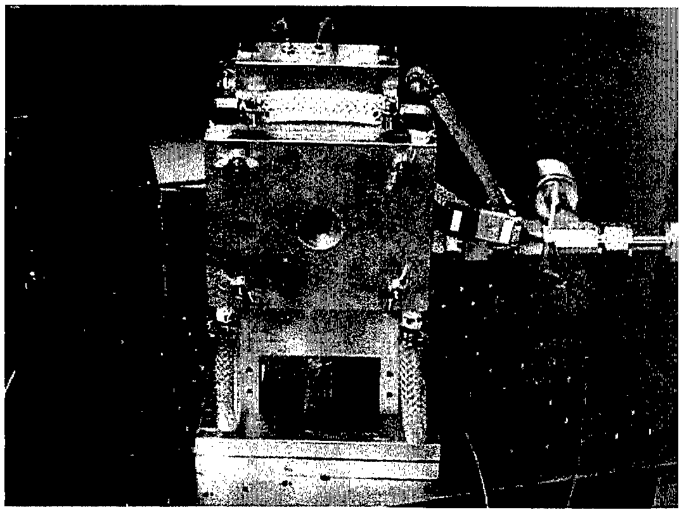


Figure 5. Vacuum Flat Pack Test Station for spectral measurements

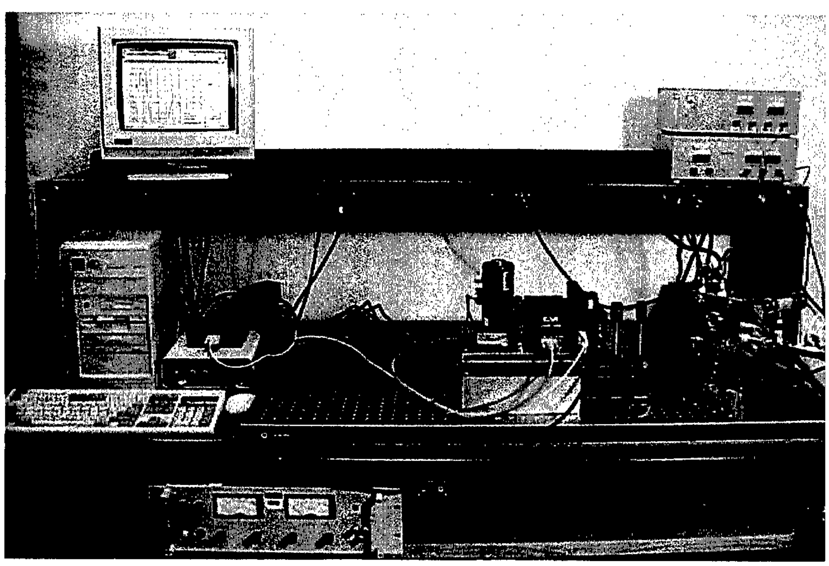


Figure 6. Optics Bench for spectral measurements (Flat Pack on right)

The first tests used 2" x 2" Kanthal coupons. Kanthal is interesting because it is a metal, which would be easier to hermetically seal to a metal base in an actual TPV system. Again, a hermetic seal is necessary to protect the tungsten from exposure to oxygen. Also, Kanthal was an easy first step for testing, because it can be electrically heated in the Vacuum Flat Pack, which is less complicated than heating the backside of a SiC coupon. The disadvantage of Kanthal is that it has an upper temperature limit near 1300° C, which is at the lower end of anticipated TPV operating temperatures. A more substantial effort was undertaken on SiC coupons, as described on the next page.

Kanthal coupons were air baked at 1200° C for preoxidation, then sputter-coated with tungsten and an AR-coating of yttria stabilized zirconia (YSZ). These were heated to 1350° C in high vacuum to test durability. After forty hours, there was no degradation evident. One of these samples is shown here in figure 7. Shown below in figure 8 is the emissivity of this coupon, as measured in the Flat Pack test station. The emissivity at longer wavelengths is higher than what had been expected, possibly because the surface of the coupon was rough. Still, this first test was a success; it showed that a durable coating could be made that displayed spectral selectivity.

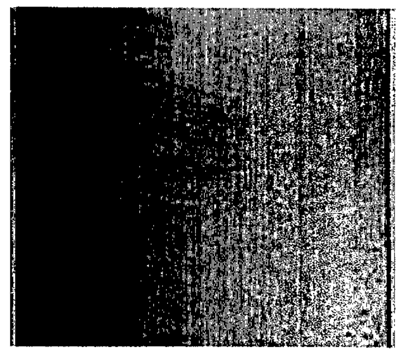


Figure 7. Kanthal coupon coated with tungsten and YSZ (actual size)

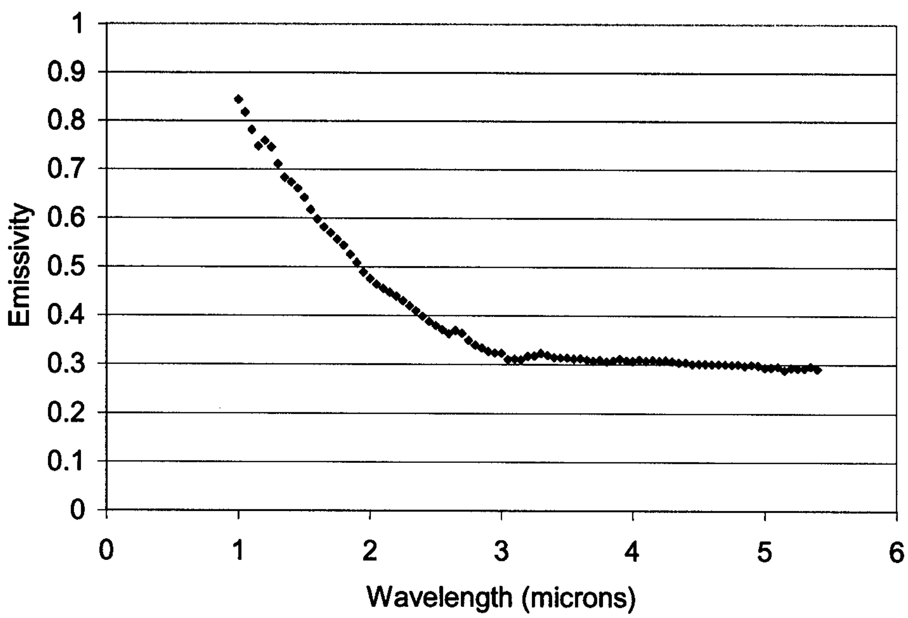


Figure 8. Emissivity of Kanthal sputter-coated with tungsten and YSZ, measured in the Flat Pack test station at 900° C

Coupons of silicon carbide (SiC) were coated with a variety of anti-reflective materials for comparison. Coupons were procured from both Hexoloy and Standard Ceramics. Coatings included YSZ, zirconia (ZrO_2) and alumina, among others. Pictured in figure 9 are coupons that were sputter-coated with tungsten, with e-beamed ZrO_2. These were heated in high vacuum to 1300° C with no apparent change. Pictured in figure 10 is the emissivity of this material. This shows more selectivity than the Kanthal coupon showed in figure 8, possibly because the SiC coupons were smoother (more specular). Similar results were achieved using the other AR coatings.

Again, these results were more promising in a qualitative sense. The coatings showed good durability and selectivity, so there was a strong likelihood that coated cylinders in a TPV system would be durable and selective. As discussed later in this report, cylinder coatings take place in different pieces of equipment. Coating rates and conditions are different, which have an effect on spectral properties. Before moving on to coating cylinders, there was a strong interest in testing the coatings at higher temperatures. A clever test was devised to do this, and is described next.

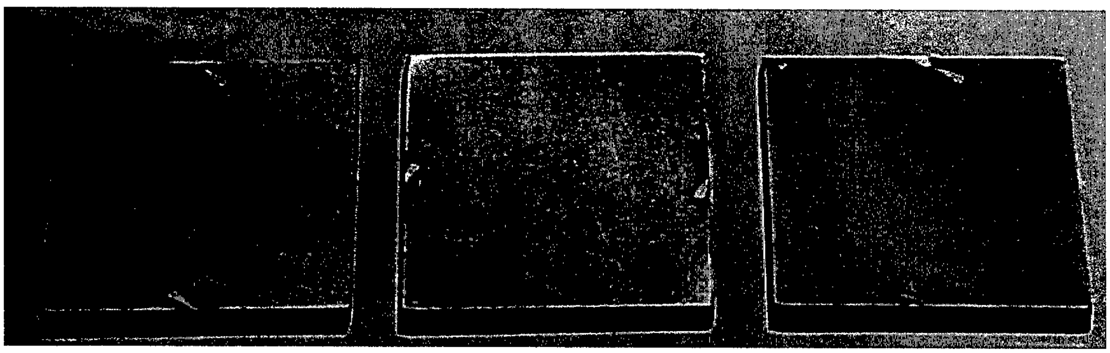


Figure 9. SiC coupons sputter-coated with tungsten, then e-beamed with ZrO_2

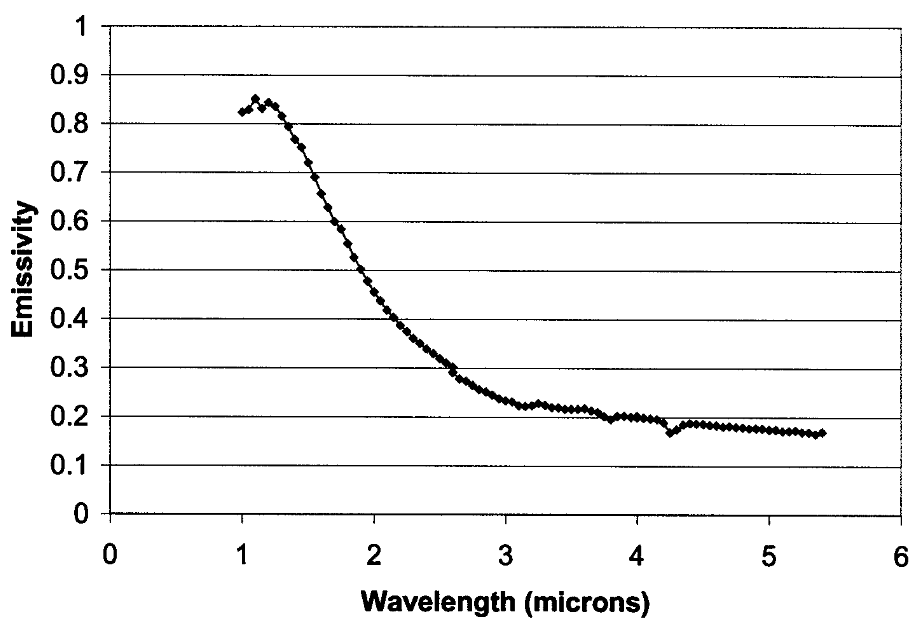
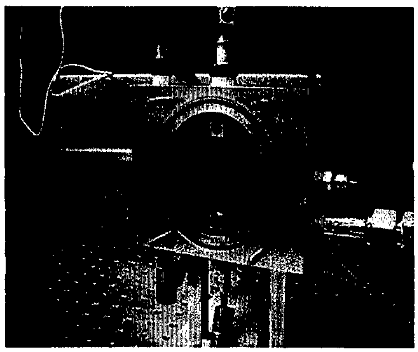


Figure 10. Emissivity of the a SiC coupon with tungsten and ZrO_2

To test the coatings at higher temperatures, a simple solution was devised. A ribbon of tungsten was AR-coated, then electrically heated in the Flat Pack. Recall that a coupon could only be heated to 1000° C, because of the limitation of the SiC hot-surface ignitors used to heat the coupons. No such constraint exists with a small ribbon. Just as a light bulb uses a thin wire of tungsten until it glows white hot, the Flat Pack can heat a ribbon of tungsten. Shown in figure 11 is the ribbon mounted in the Flat Pack, and a shot of the unit in operation. Figure 12 shows the spectrum from this test. The AR-coating proved to be durable at a temperature of 1300° C, and the emissivity drops off at longer wavelengths. Temperatures were taken with a thermocouple welded to the backside of the ribbon. Operation at high temperature flattens out the emissivity of the underlying tungsten, so the spectrum does not drop off as sharply as the theory shown in figure 2, but impressive spectral selectivity is still evident.



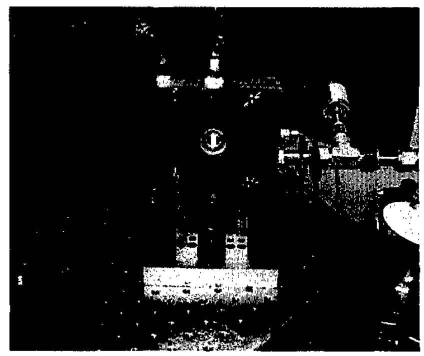


Figure 11. Vacuum Flat Pack modified for tungsten ribbon; note glowing ribbon through viewport in the picture on the right

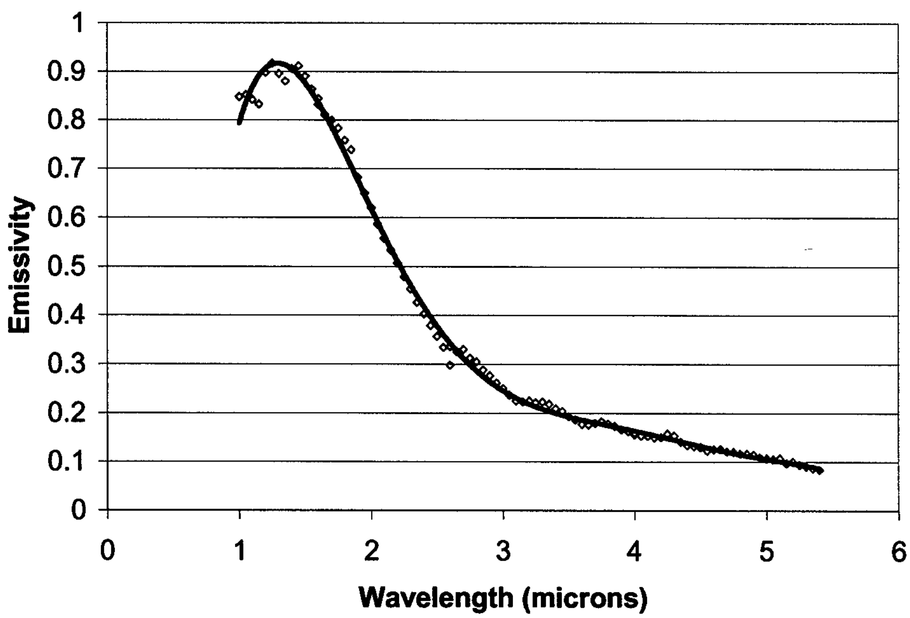


Figure 12. Emissivity of AR-coated tungsten ribbon at 1300° C

AR/RM Cylinder Coatings

Under an Army SBIR Phase II contract, JX Crystals is developing a 200 Watt TPV system. The deliverable unit under that contract seemed to be an excellent platform for a demonstration of the new emitter coating technology. So, the Army Research Office contract did not stop at coupon experiments; it included the development of coatings on cylinders appropriately sized for the TPV unit being made for the Army SBIR contract.

Sputter-coating emitter cylinders measuring 14" long required the purchase of the refurbished MagDrum Sputtering system shown in figure 13. JX Crystals purchased this system and began operating it in February, 2000. It has been used for tungsten depositions and AR-coatings (alumina). The throughput of this system is quite high; the company can process six emitters at a time, and probably four runs per day. So, the company has an emitter capacity in the range of 1,400 per year.

Surrounding the emitter in the Army SBIR TPV system is a quartz tube, allowing the emitter to operate in a vacuum or an inert gas atmosphere. It is desirable to coat the outside of this quartz tube with a filter, to reject some of the unusable longer wavelengths back to the emitter (particularly in the 2-3 micron range). A rotisserie was designed for one of the company's e-beams, allowing JX Crystals to deposit simple dielectric filters. This system is shown in figure 14; note the bell jar at right that comes down over the e-beam, and the wheel at left that goes on top of the rotisserie to rotate the tube. Fairly uniform filter coatings on quartz cylinders have been achieved with this system.

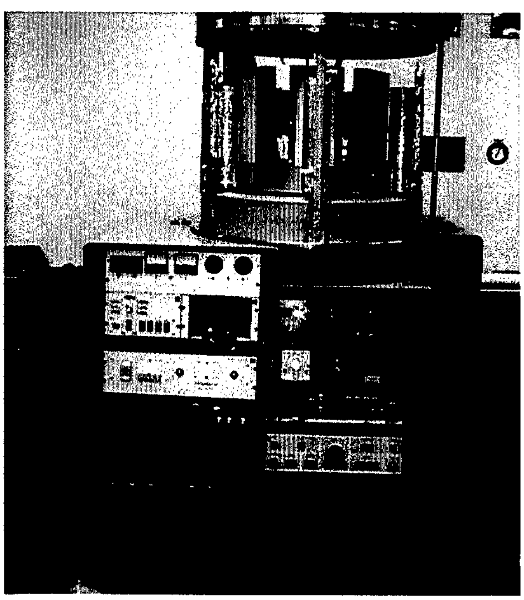


Figure 13. JX Crystals' MagDrum Sputtering system for cylinder coatings

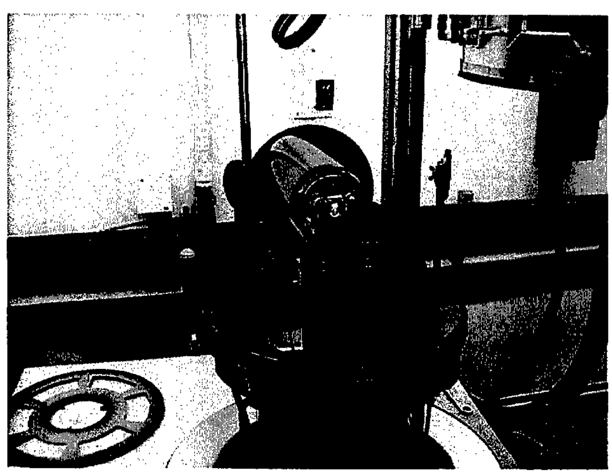


Figure 14. Rotisserie for filter coatings in the company's e-beam

It was important that the company verify that the sputter-coated cylinders display the same sort of selectivity that had been seen in the coupon and ribbon testing. Unfortunately, JX Crystals is not equipped to measure the emissivity of an operating cylinder; at present, the Flat Pack is the only way that the company can make those measurements. To get around this restriction, the company tied down a tungsten ribbon over a small cylinder, then sputtered tungsten and an AR-coating onto the cylinder with the new MagDrum Sputtering system. Then, the ribbon was taken off and measured in the Flat Pack at 1300° C, in the same way described earlier. The expected results were attained, and are shown in figure 15.

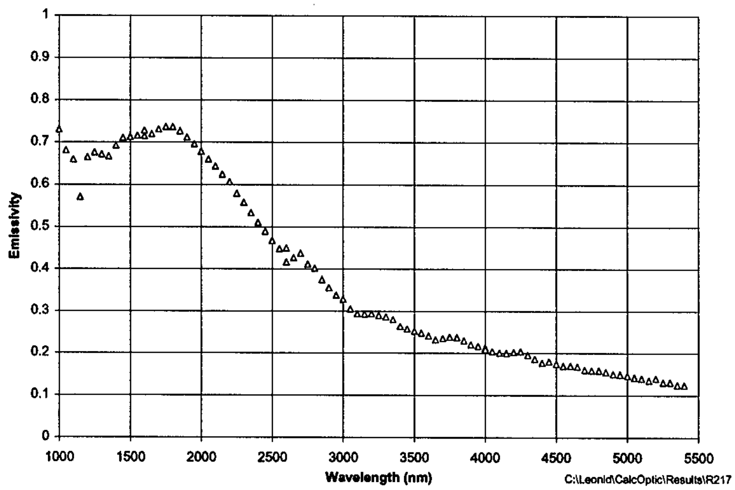


Figure 15. Emissivity at 1300° C of AR-coated tungsten deposited in the MagDrum Sputtering system

The next concern with coated cylinders was how they would perform in operating TPV systems. In particular, a test was required to determine whether the cavity in which the emitter operates could be properly evacuated, then backfilled with an inert gas. While the company waited for delivery of the MagDrum, it devised a test for evacuation and backfill. A sheet of tungsten foil was AR-coated, then wrapped around a Kanthal cylinder. If the evacuation and backfill was unsuccessful with such a test, only the foil "sleeve" would be lost. This set-up is shown in figure 16, and proved successful. The large tube coming off of the base at the left is used for pumping down the cylinder (removing air), and for backfilling with Argon gas. Part of the burner assembly is visible underneath, and is the subject of the next section. The remainder of this section discusses cylinder coatings.

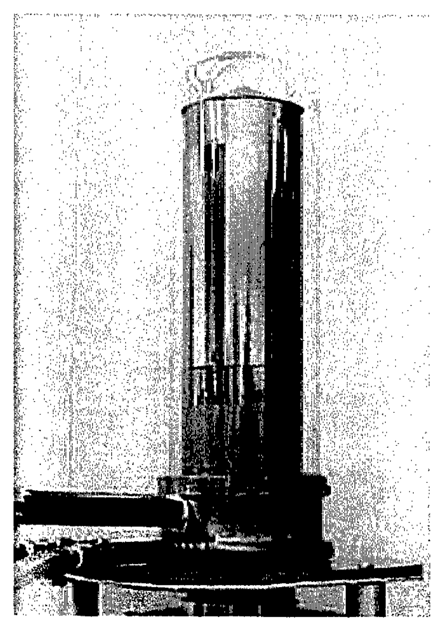


Figure 16. Tungsten sleeve over a Kanthal cylinder

The MagDrum Sputtering system is fully operational. Pictured in figure 17 are two coated emitters: SiC on the left and Kanthal on the right. Uniform coatings have been achieved with a variety of AR-coatings, and a cylinder has been run at operating temperatures for an hour with no apparent degradation. Figure 18 shows the unit in operation at 1300° C, with a test cell mounted on the far side for power measurements (results provided in the following pages). A cooling fan is located over the top of the operating unit. This unit is operating with a filter-coated quartz tube over it, and the emitter glows brightly enough to see it through the filter. The filter-coated quartz tube is shown in figure 19, ready for operation. Figure 20 provides the filter spectra before and after the one hour run; the filter was still intact and operational. The test was quite successful, particularly in terms of the two most important critereon: cell power output and system efficiency.

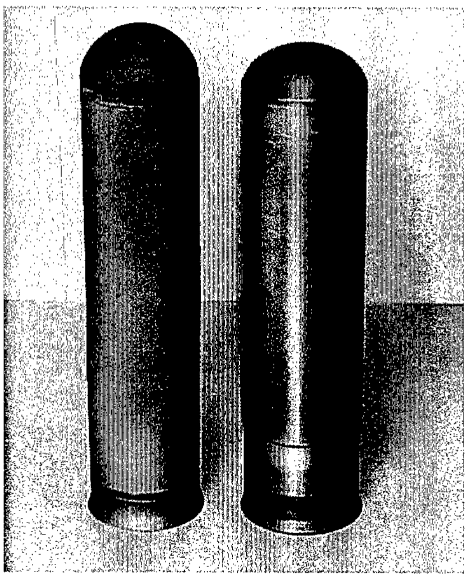


Figure 17. SiC and Kanthal cylinders coated in the MagDrum

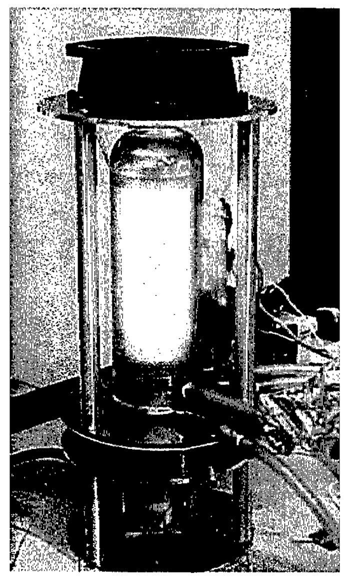


Figure 18. Operating TPV system with filter and test cell (behind at right)

Figure 19. Filter in place

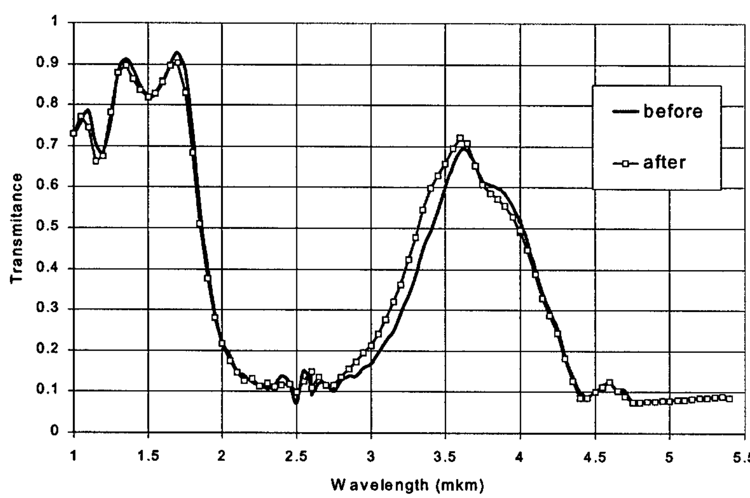


Figure 20. Filter spectra before and after one hour

Burner Development

The burner used for the cylinder testing uses propane, which is relatively easy to burn at the required temperatures. The Army is particularly interested in burners that utilize JP8 fuel, which is one important focus of the company's Army SBIR contract discussed previously. Under that contract, JX Crystals is doing system development, and Thermo Power Corp. is doing the JP8 burner design. That burner has been designed to fit into the existing system; system integration is scheduled for early fall, 2000.

Pictured in figure 21 is the burner/emitter/recuperator design presently in use. Propane and air are premixed, then combusted along with a secondary air flow. Combustion occurs inside the inner SiC tube (the "radiator"). Then, the combustion gases flow back down, between the radiator and the inside of the "IR emitter," which is the coated cylinder discussed throughout this report. The exhaust gas runs through a recuperator to preheat the secondary combustion air. Figure 22 shows a TPV system in operation with a quartz tube (without a filter coating). The burner housing is visible under this operating unit.

Some of the stainless steel burner elements were only able to tolerate operating temperatures for the extent of the one hour test; those parts are being remade using inconel.

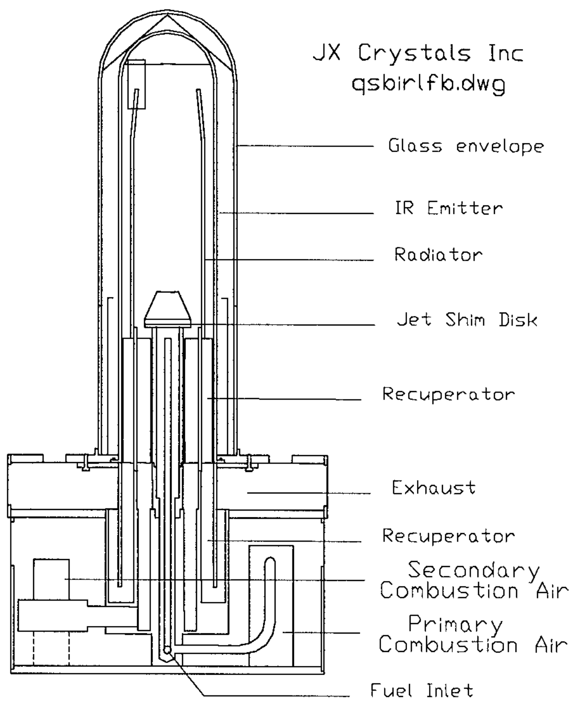


Figure 21. Burner/Emitter/Recuperator design for a TPV system

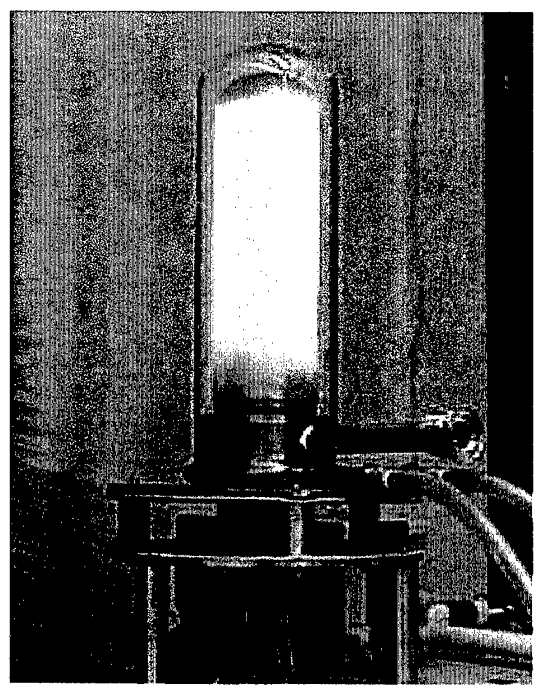


Figure 22. Operating burner without a filter coating on the quartz tube

Test Results

The test cell mounted next to the glowing emitter in figure 18 provided the results that were anticipated at this contract's inception. This particular GaSb cell has been qualified by NASA, so the company has an accurate quantum efficiency measurement for the cell. Only with a spectrally selective emitter could the company hope to get strong power output from the cell, and that was achieved. This cell put out 1.27 Watts; results are shown below in figure 23. A full "Photovoltaic Converter Array" (PCA) surrounding one of the emitters made under this contract has 360 GaSb cells. While the company's Army SBIR contract calls for development of a 200 Watt TPV unit using the 360 cell PCA, it appears that as much as 457 Watts can be attained. This is a stunning achievement. The estimated power consumption for the cooling fan and combustion air system is approximately 110 Watts, so the net output power could be in the range of 350 Watts.

The one hour test revealed two system weaknesses, both of which can be solved. First, as mentioned earlier, some of the stainless steel burner elements degraded over the length of the test. So, these parts are being remade using inconel. In the meantime, this meant that another test was likely to be cut short by a part failure in the burner.

The second system weakness was in the seal, which was anticipated. The company has submitted a proposal to address this problem. Simply put, light bulb technology is not trivial. To operate an emitter with a tungsten coating, all of the air has to be evacuated from the cavity around the emitter. JX Crystals was able to make a tight enough seal from the quartz tube to the base and the emitter to the base to do this. Then, the cavity was backfilled with Argon. After the one hour test run, the seal slipped and was no longer tight enough to evacuate the cavity, so the experiment was shut down.

Since the next proposed effort is to develop a better seal, it seemed wasteful to spend time trying to get the present seal to be functional for one more test. So, a test with the fully populated PCA was deferred until development of the seal discussed at the end of this report.

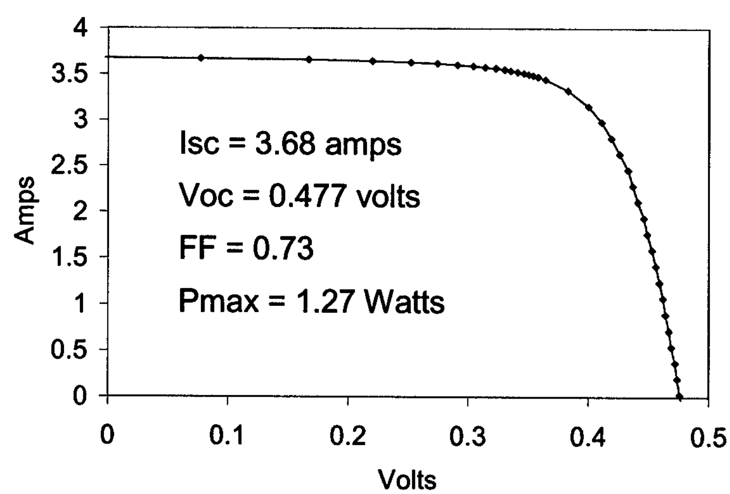


Figure 23. Current vs. Voltage curve for the GaSb test cell from figure 18

Conclusions and Relation to Future Work

The goals of this contract were:

- Fabricate AR coated / refractory metal coated / SiC test coupons
- Measure coupon spectral performance and durability
- Procure and install sputter deposition system for cylinder coatings
- Deposit coatings on cylinders
- Design, build, and test emitter thermos
- Test coated cylinders in TPV test system with PCA

As has been described, the goals were met with very positive results. The proposed effort to further this technology is very close to commencing; it has passed through DARPA review and is currently being reviewed by the Army Research Office.

The system design for the hermetically sealed emitter "thermos" is shown in figure 24, along with the system design including the PCA. Design details are available in the proposal, and not repeated here. The tasks for the proposed effort are:

- Design and procure parts for AR/RM emitter thermos
- Deposit AR and RM coatings
- Develop sealing technique and assemble thermos
- Integrate and test hermetically sealed AR/RM thermos
- Redesign electrically heated emitter/PCA test system
- Upgrade existing test system
- Measure PCA efficiency and emitter spectra
- Report

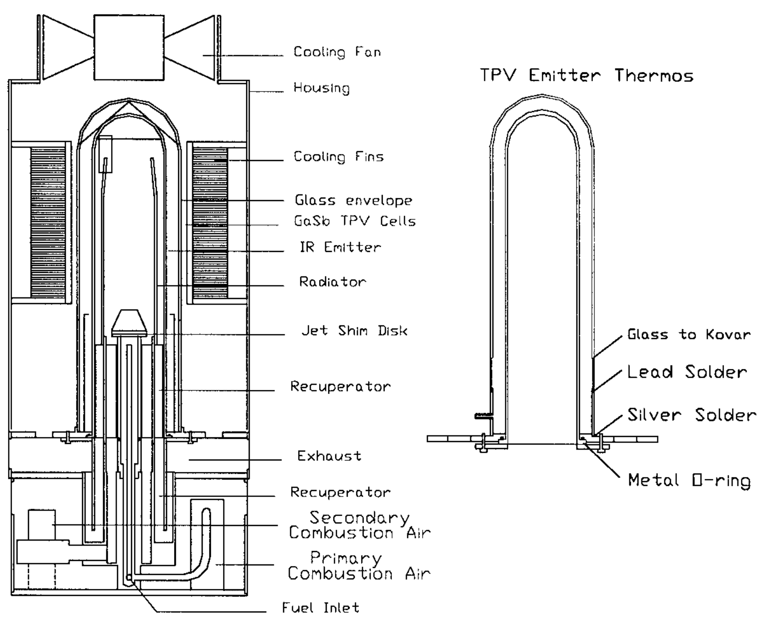


Figure 24. Hermetically sealed TPV system design, with emitter thermos detail

As discussed earlier in this report, the coated cylinders are appropriately sized for the TPV unit being built under the company's Army SBIR Phase II contract. The new contract that the company anticipates for the hermetically sealed emitter thermos makes it possible to incorporate coated emitters into the Army SBIR unit.

How the new hermetic seal contract would relate to the existing Army SBIR contract is outlined below.

<u>Hermetic Seal Contract</u>

- Develop hermetically sealed emitter thermos
- Fabricated two HSET's
- Improve data collection capability
- Fabricate 200 Watt propane demo (using existing PCA and burner)

<u>Army SIBR II</u>

- Fabricate liquid fuel burner (Thermo Power)
- Fabricate PCA
- Fabricate emitter (now using one of the HSET's)
- Fabricate and deliver JP8-fired 200 Watt TPV generator

The anticipated performance from the delivered system is that the burner will be 75% efficient, that 74% of the emitted spectrum will be <1.8 microns, and that 28% of that energy will be converted into electricity. That multiplies to 16% efficiency. Parasitic losses (power to run the blowers) and view factor (10% of the radiant energy does not get received by the cells) result in a net efficiency of 10% at 1300° C. This will be a major advancement in thermophotovoltaic technology.